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ELECTRON CORRELATION IN METALS

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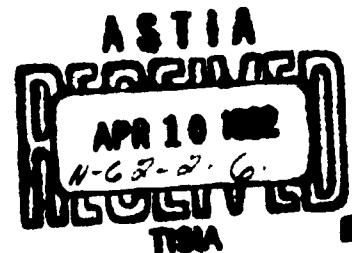
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Abstract

We report here some new results we have obtained for the
diagonal element of the second-order density matrix (pair function)
and for the momentum distribution of an interacting electron gas.
In the low density limit, the pair function has been discussed
previously by March and Young (1959) and it is shown here that,
to a similar degree of approximation, the first-order density
matrix and hence the momentum distribution may be obtained.   In
the high-density problem, the pair function has also been
calculated using the Green's function approach and this result
complements the calculation of the momentum distribution carried
out recently by Daniel and Vosko (1960).   From the information
thus available in these high and low density limits, the range
of usefulness of the concept of the Fermi surface in an
interacting electron gas is discussed.

Also, results of variational calculations on the stability
of Overhauser spin-density waves in metals are reported.   It is
concluded that such waves reduce the energy below the Hartree-
Fock value only when the interaction becomes very strong, or
equivalently when the density is very low.

Some preliminary work on the correlation problem in a
non-uniform electron gas is also briefly discussed.

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1. Introduction

As we discussed in ASR No. 1, the problem of dealing with the Coulomb interactions between conduction electrons in metals has proved very formidable and no complete solution has, as yet, been found. In recent years, beginning with the important investigation of Macke (1950), attention has been focused primarily on the use of perturbation theory. Unfortunately, the perturbation expansion does not prove useful in practice in the range of real metallic densities, which are characterized by the usual gas parameter r_s lying in the range $2 < r_s < 5.5$.

As we emphasized in ASR No. 1, in attempting to understand the correlation problem, it is often useful to consider a wider range of densities than that represented above, and in particular to consider the formal limiting cases $r_s \to 0$ and $r_s \to \infty$. The first case represents the domain of perturbation theory based on plane waves, but the second case has been less fully discussed. For this reason, we have extended the earlier work by March and Young (1959) on the diagonal element of the second-order matrix (pair function) and have thereby obtained the first-order density matrix and momentum distribution in this limit of low density. The results of this calculation are reported in §3 after a brief summary of the results of the Hartree-Fock approximation in §2. In §4, the other extreme limit of high density is discussed. In order to facilitate the calculations in this limit, a generalization of the concept of density matrices proves desirable as we

emphasized in §2 of ASR No. 1. The appropriate tools are then found to be the first and second-order Green's functions familiar to field theorists. A calculation is reported which yields the pair function in the high-density limit: uniform application of this same method leads, in addition, to results in agreement with those of Daniel and Vosko (1960) for the momentum distribution. By analysis of these limiting forms for high and low density it is shown in §5 that information may be obtained on the range of usefulness of the concept of a Fermi surface in metals.

In §6 we report the final results of a variational calculation carried out by one of us (N.H.M.) in conjunction with M. I. Darby and W. H. Young. This was designed to examine the stability of Overhauser spin-density waves in metals. The results provides strong evidence that such waves are only energetically favoured for very strong interactions, or equivalently, for very low densities. They appear therefore to have no relevance to the correlation problem for real metallic densities.

Finally, in §7, we report some preliminary findings on the proton lattice, in both high and low density limits.

2. Hartree-Fock pair function and first-order density matrix

We briefly recall here that our problem is basically to calculate the ground state wave function $\Psi(\underline{x}_1 \underline{x}_2 \cdots \underline{x}_N)$ for

a system of N electrons, where $\underline{x}_1$ denotes the space co-ordinates $\underline{r}_1$ and the spin co-ordinates σ_1, from the Schrödinger equation

$$H\psi = \epsilon\psi \qquad (2.1)$$

where the Hamiltonian H is given in full in equation (2.1) of ASR No.1. As stressed in that report, it is often both convenient, or more important, conceptually very fruitful, to work with first and second-order spinless density matrices $\gamma(\underline{r}_1'\underline{r}_1)$ and $\Gamma(\underline{r}_1'\underline{r}_2'\underline{r}_1\underline{r}_2)$ defined by the equations

$$\gamma(\underline{r}_1'\underline{r}_1) = N \int \psi^*(\underline{r}_1'\sigma_1\underline{x}_2\ldots\underline{x}_N)\psi(\underline{r}_1\sigma_1,\underline{x}_2\ldots\underline{x}_N)d\sigma_1\, d\underline{x}_2\ldots d\underline{x}_N \quad (2.2)$$

$$\Gamma(\underline{r}_1'\underline{r}_2'\underline{r}_1\underline{r}_2) = \frac{N(N-1)}{2} \int \psi^*(\underline{r}_1'\sigma_1\underline{r}_2'\sigma_2\underline{x}_3\ldots\underline{x}_N)\psi(\underline{r}_1\sigma_1\underline{r}_2\sigma_2\underline{x}_3\ldots\underline{x}_N)$$

$$d\sigma_1\, d\sigma_2\, d\underline{x}_3\ldots d\underline{x}_N \qquad (2.3)$$

We note now that the diagonal elements of γ and Γ have direct physical interpretations. Thus $\gamma(\underline{r}_1\, \underline{r}_1)$ gives the particle density which in the Sommerfeld model is simply the constant $3/4\pi r_s^3$, while $\Gamma(\underline{r}_1\underline{r}_2\underline{r}_1\underline{r}_2)$ is effectively the probability of electron separation or the pair distribution function. Then, as Mayer (1955) was the first to show, the energy per particle ϵ/N is given by

$$\frac{\epsilon}{N} = -\left(\frac{3}{2\pi r_s^3}\right)^{-1} \left[\nabla^2_{\underline{r}}\, \gamma(\underline{r}'\underline{r})\right]_{\underline{r}'=\underline{r}} - \frac{3}{2r_s^3}\int_0^\infty (1 - F(\zeta))\zeta\, d\zeta \quad (2.4)$$

where $F(\zeta) = F(|\underline{r}' - \underline{r}|)$ is the pair function, normalized to unity for large $|\underline{r}' - \underline{r}|$.

When the total wave function is a determinant of plane waves, we have the usual Hartree-Fock forms

$$\gamma(\underline{r}'\underline{r}) = \frac{k_f^3}{\pi^2} \frac{j_1(k_f|\underline{r}' - \underline{r}|)}{k_f|\underline{r}' - \underline{r}|} \qquad j_1(\rho) = (\sin \rho - \rho \cos \rho)/\rho^2 \qquad (2.5)$$

$$F(\underline{r}'\underline{r}) = 1 - \frac{9}{2} \left\{ \frac{j_1(k_f|\underline{r}' - \underline{r}|)}{k_f|\underline{r}' - \underline{r}|} \right\}^2 , \qquad (2.6)$$

where k_f is the magnitude of the wave vector at the Fermi surface and is related to the mean interparticle spacing by

$$k_f \, r_s = \left(\frac{9\pi}{4}\right)^{\frac{1}{3}}. \qquad (2.7)$$

Using atomic units, it follows from (2.5) and (2.6) that the energy per particle is

$$\frac{\epsilon}{N} = \frac{3}{10} \left(\frac{9\pi}{4}\right)^{\frac{2}{3}} \frac{1}{r_s^2} - \frac{3}{4\pi} \left(\frac{9\pi}{4}\right)^{\frac{1}{3}} \frac{1}{r_s} . \qquad (2.8)$$

3. Pair function and first-order matrix in low-density limit

The low-density form of the pair function has been discussed earlier by March and Young (1959) using the electron lattice model of Wigner (1938). We simply summarize the results by saying that as r_s becomes very large, the electrons relative to a given particle we have singled out, and placed at the origin of co-ordinates sit

on the sites of a body-centred cubic lattice. As r_s is then reduced somewhat, the electrons can be thought of as represented by harmonic oscillator functions

$$\psi = \left(\frac{\alpha}{\pi}\right)^{\frac{3}{4}} \exp\left(-\frac{\alpha r^2}{2}\right); \quad \alpha = r_s^{-\frac{3}{2}}. \qquad (3.1)$$

The results obtained by March and Young (1959) for the pair function are represented in curves 1 and 2 of Fig. 1, for cases r_s = 100 and r_s = 4. For comparison, the Fermi hole result given in (2.6) is also shown in curve 3. We emphasize that while curve 1 should be reliable, curve 2 represents an extrapolation beyond the range of validity of the low density form (3.1), and is given solely to show the qualitative influence of varying r_s.

We shall now indicate how this work may be generalized to yield the first-order density matrix and momentum distribution for a low-density gas. From the orbitals (3.1), centred on each lattice site, we build a Dirac density matrix. This will not, of course, contain the condition of translational invariance, that is the diagonal element will not be a constant. To obtain a result consistent with the Sommerfeld model we must average over all positions, and then the desired first-order density matrix is easily shown to be

$$\gamma(\underline{r}'\underline{r}) = \frac{k_f^3}{3\pi^2} \exp\left(-\frac{\alpha}{4}|\underline{r}' - \underline{r}|^2\right). \qquad (3.2)$$

The form (3.2), as is easily seen, satisfies all the essential conditions, but its range of validity is, of course, restricted,

as we shall discuss below. Nevertheless, in conjunction with the high density results of §4, it may be used to draw some interesting conclusions about the Fermi surface (see §5).

At this stage, it is enlightening to examine the momentum distribution corresponding to the first-order matrix (3.2), and this may be found as follows: We require the occupation numbers $P(\underline{k})$ of plane wave states $V^{-\frac{1}{2}} e^{i\underline{k}\cdot\underline{r}}$, where V is the volume of the metal and thus we write

$$\gamma(\underline{r}'\underline{r}) = \frac{2}{V} \sum_{\underline{k}} P(\underline{k})e^{-i\underline{k}\cdot\underline{r}'} e^{i\underline{k}\cdot\underline{r}}, \tag{3.3}$$

or remembering that the density of states in $\underline{k}$ space is $(1/8\pi^3)V$ and using Bauer's expansion for a plane wave as a series of spherical waves:

$$\gamma(\underline{r}'\underline{r}) = \frac{1}{4\pi^3} \int_0^\infty P(k) \frac{\sin k|\underline{r}' - \underline{r}|}{k|\underline{r}' - \underline{r}|} 4\pi k^2 \, dk. \tag{3.4}$$

It is convenient at this point to measure k in units of the Fermi momentum k_f, that is we write $K = k/k_f$, and then (3.4) becomes

$$\gamma(\underline{r}'\underline{r}) = \frac{k_f^3}{\pi^2} \int_0^\infty P(K) \frac{\sin k_f K|\underline{r}' - \underline{r}|}{k_f K|\underline{r}' - \underline{r}|} K^2 dK. \tag{3.5}$$

Inverting this relation and using (3.2) for $\gamma(\underline{r}'\underline{r})$ we find

$$P(K) = \frac{3\pi^{\frac{1}{2}}}{r_s^{\frac{3}{2}}} \exp\left\{-\left(\frac{9\pi}{4}\right)^{\frac{2}{3}} r_s^{-\frac{1}{2}} K^2\right\}, \tag{3.6}$$

where we have eliminated k_f using (2.7). As we have remarked earlier, the range of validity of (3.6) is restricted, because the orbitals ψ on different lattice sites have been assumed orthogonal, whereas this is only rigorously true in the limit $r_s \to \infty$. However, a rough estimate of the range of validity may be obtained by noting that the occupation numbers $P(K)$ must always lie between 0 and 1. Since $P(K)$ as given by (3.6) has its maximum at $K = 0$, we must have that

$$\frac{3\pi^{\frac{1}{2}}}{r_s^{\frac{3}{2}}} < 1 \qquad (3.7)$$

$$\text{or} \quad r_s > 9 \cdot 3.$$

The kinetic energy per particle, in the approximation implied by (3.6) is easily shown to be

$$\frac{T}{N} = \frac{3}{4r_s^{\frac{3}{2}}} , \qquad (3.8)$$

in agreement with Wigner (1938). La·er treatments based on more careful study of the dynamics of the vibrating electron lattice (Coldwell-Horsfall and Maradudin, 1960; Carr, 1961) change (3.8) somewhat, but will not affect the overall validity of the argument presented above. We note finally for the low-density limit, that the momentum distribution is of classical 'Maxwell-Boltzmann' form: this is in sharp contrast to the high density results to which we now turn.

4. Pair function and first-order density matrix in high-density limit

Using the perturbation theory of Gell-Mann and Brueckner (1957) in suitable form, we shall now discuss the way in which the pair function and the first-order density matrix develop from the Hartree-Fock forms given in §2, equations (2.6) and (2.5). In order to do so it is very convenient to introduce a generalization of density matrices to include also the time: this will greatly facilitate the setting up of useful equations from which the matrices can be determined. We discussed this situation fully in §2(iii) of ASR No. 1, where we pointed out that the first and second order Green's functions constitute the desired generalizations of the density matrices. In fact, equations (2.38) and (2.39) of ASR No. 1 give the explicit relations between the Green's functions and the density matrices. The basic equation for the second-order Green's function (see (2.35) of ASR No. 1) may be written in the form

$$G(x_1 x_2 x_3 x_4) = G(x_1 x_3)G(x_2 x_4) - G(x_1 x_4)G(x_2 x_3)$$

$$+ \int d^4 y_1 \, d^4 y_2 \, d^4 z_1 \, d^4 z_2 \; G(x_1 y_1)G(x_2 y_2)I(y_1 y_2 z_1 z_2)G(z_1 z_2 x_3 x_4).$$

$$(4.1)$$

In the high density limit it now appears possible to make progress in the electron gas problem by inserting the first approximation for $G(x_1 x_2 x_3 x_4)$ inside the integral, provided we approximate sufficiently carefully to the interaction operator. The procedure to be adopted was outlined in §4(iii) of ASR No. 1, and we have

now carried through the calculations in detail, as described below.
The basic equations of the treatment we shall employ are (4.25) and
(4.26) of ASR No. 1. The method used is to seek the Fourier
transform of the two-particle Green's function, which is closely related
to the second order density matrix (see (2.39) of ASR No. 1).
We therefore write the interaction

$$v(r) = \frac{e^2}{r} = \frac{1}{V} \sum v(k) \, e^{ik \cdot r} \tag{4.2}$$

and then it follows that

$$v(k) = \frac{4\pi e^2}{k^2} \tag{4.3}$$

Furthermore we develop $G_0(rt)$, which enters the Green's function
equation for the two-spin case, namely,

$$G(\underline{r}t\underline{r}'t\underline{r}t''\underline{r}'t'') = G_0(\underline{r}t \ \underline{r}t'')G_0(\underline{r}'t\underline{r}'t'') - \tfrac{1}{2} G_0(\underline{r}t\underline{r}'t'')G_0(\underline{r}'t\underline{r}t'')$$

$$- \int d^4y_1 \, d^4y_2 \, G_0(\underline{r}ty_1)G_0(\underline{r}'ty_2)V(y_1-y_2)G_0(y_1\underline{r}t'')G_0(y_2\underline{r}'t'')$$

$$+ \tfrac{1}{2} \int d^4y_1 \, d^4y_2 \, G_0(\underline{r}ty_1)G_0(\underline{r}'ty_2)v(y_1-y_2)G_0(y_1\underline{r}'t'')G_0(y_2\underline{r}t''), \tag{4.4}$$

in the form

$$G_0(rt) = \frac{1}{2\pi V} \sum_k \int_{-\infty}^{\infty} G_0(k\epsilon)e^{i(k \cdot r - \epsilon t)} \, d\epsilon$$

$$= \frac{1}{V} \sum_{\underline{k}} G_0(kt)e^{ik \cdot r} \tag{4.5}$$

After some calculation it may then be shown that

$$
\begin{aligned}
G_0(kt) &= -ie^{-ik^2/2\,t} && t < 0 \quad k > 0 \\
&= ie^{-ik^2/2\,t} && t > 0 \quad k > 1 \\
&= 0 && t < 0 \quad k > 1 \\
&&& t > 0 \quad k < 1
\end{aligned} \tag{4.6}
$$

Also it is known that equation (4.25) of ASR No. 1 for the modified interaction V may be solved by Fourier analysis, and writing

$$
V(y_1-y_2) = \frac{1}{2\pi v} \int \sum_k v(q\omega)\, e^{iq(r_1-r_2)-i\omega(t_1-t_2)}\, d\omega \tag{4.7}
$$

the solution is

$$
v(q\omega) = \frac{2\pi\alpha r_s}{q^2[1 + \frac{\alpha r_s}{\pi^2 q^2} Q_0(q\omega)]} \tag{4.8}
$$

where

$$
Q_0(q\omega) = \int_{\substack{|k|<1 \\ |k+q|>1}} d^3k \left\{ \frac{1}{\omega - (q^2/2 + q\cdot k) + i\delta} - \frac{1}{\omega + (q^2/2 + q\cdot k)+i\delta} \right\}. \tag{4.9}
$$

This latter function $Q_0(q\omega)$ has been discussed earlier by DuBois (1959).

If we now denote the correction to the Hartree-Fock result for $G(rt\ r't\ rt''\ rt'')$ by G_{bg}, then we may write

$$G_{bg}(rt\ r't,\ rt''\ r't'') = \frac{1}{(2\pi)^3} \int dq\ e^{iq(r - r')}\ G_{bg}(q,\ t - t'')$$

$$= \int d^4y_1\ d^4y_2\ G_0(rt,\ y_1)\ G_0(r't\ y_2)\ V(y_1 - y_2)\ G_0(r_1rt'')G_0(r_2r't'')$$

$$= \frac{1}{(2\pi)^{12}} \int dk\ d\epsilon\ dk'\ d\epsilon'\ dq\ d\omega\ e^{iq(r-r') - i(\epsilon+\epsilon')(t'- t'')}$$

$$\times G_0(k\epsilon)\ G_0(k - q,\ \epsilon - \omega)\ v(q\omega) \tag{4.10}$$

If we let $t'' \to t^+$ at this stage we obtain

$$G_{bg}(q) = \frac{1}{(2\pi)^9} \int dk\ d\epsilon\ dk'\ d\epsilon'\ d\omega\ G_0(k\epsilon)\ G_0(k - q,\ \epsilon - \omega)$$

$$v(q\omega)\ G_0(k'\epsilon')\ G_0(k' + q,\ \epsilon' + \omega)$$

$$= - \frac{1}{(2\pi)^7} \int Q_0{}^2(q\omega)\ v(q\omega)\ d\omega. \tag{4.11}$$

Substituting for $v(q\omega)$ we obtain the final result

$$G_{bg}(q) = - \frac{1}{(2\pi)^4} \int_{-\alpha}^{\alpha} d\omega\ \frac{Q_0{}^2(q\omega)\ \alpha r_s/\pi^2 q^2}{1 + (\alpha r_s/\pi^2 q^2)\ Q_0(q\omega)} \tag{4.12}$$

Further progress calls for the use of numerical methods and this aspect of the work is now being planned.

5. The Meaning of a Fermi surface

The fact that we can obtain the momentum distribution in two limiting cases has interesting implications. For, as the work of Daniel and Vosko has shown, the discontinuity in $P(K)$ at the

Fermi surface for $r_s = 0$ is not removed but only reduced as the density is lowered.   While this result seems not to have been established rigorously outside perturbation theory, there seems strong empirical evidence from the sharpness of the Fermi surface in real metals that such a discontinuity does in fact persist. However, our low density treatment $r_s \to \infty$ could equally well be made the basis of a perturbation treatment, and no sign of the discontinuity would then occur.   Thus, the evidence seems clear that as we follow the momentum distribution as it develops from the two limiting cases of small and large r_s there must come a critical coupling strength, or a critical density, at which the discontinuity in the momentum distribution is reduced to zero. For lower densities, it then appears that the concept of a Fermi surface will no longer be useful.   We believe at present that the critical value, r_c say, will lie outside the range of real metallic densities, or in other words that r_c will exceed 5·5.   No quantitative evaluation has so far proved possible however. Questions also remain as to the nature and order of the 'transition' occurring at r_c.   We do not expect that the pair function will undergo any marked changes at r_c and probably, to obtain a clear picture of the transition, it will eventually prove necessary to examine the third and higher-order density matrices.

Finally, to give an indication of the change in the momentum distribution as the density is varied, we have plotted in curve 1

of Figure 2 results for P(K) as given by Daniel and Vosko for the high density values ($r_s \doteq 2$) and by (3.6) for the low density region.   Curve 2 for $r_s = 16$ should be viewed with some caution, but the result for $r_s = 100$ (curve 3) should represent a good approximation.   The great difficulty, as we have stressed, is to obtain a sufficiently good approximation to the ground state in the region $2 < r_s < 5 \cdot 5$ and to locate the critical value of r_s with precision.

6. Stability of spin density waves in metals (with M. I. Darby and
   W. H. Young)

     We record here the final results of the calculations of M. I. Darby, one of us (N.H.M.) and W. H. Young bearing on the spin density waves of Overhauser (1960).   The analysis was set out in ASR No. 1 and more accurately (avoiding a sphere approximation made earlier) in section 2 of TSR No. 4.   However, evaluation of the potential energy given in equation (3) of that Report indicated that the term in a^2 in the potential energy was exceedingly small.   Examination of the reasons for this led to the use of an alternative variational function which proved much more accurate.

     Using the notation of ASR No. 1, the transformation function $\underline{R}(\underline{r})$ was taken as having components

$$R_i = x_i + \frac{a}{\alpha} \sin \alpha \; x_i \left({i = 1, 2, 3; \atop \alpha = 2\tfrac{2}{3}\pi} \right) \qquad (6.1)$$

and then in place of equation (1) of TSR No. 4, we easily find for the increase in the kinetic energy per particle:

$$\frac{\Delta T}{N} = + \frac{3a^2}{\lambda^2} \left\{ \frac{(3\pi^2)^{\frac{1}{3}}}{10} \frac{3}{2} + \frac{\alpha^2}{16} \right\} = \frac{6 \cdot 055 a^2}{\lambda^2} \qquad (6.2)$$

where

$$\lambda = \left(\frac{4\pi}{3}\right)^{\frac{1}{3}} r_s .$$

Similarly the change in the potential energy per particle is given by

$$\frac{\Delta V}{N} = - \frac{0 \cdot 0324 a^2}{\lambda} \qquad (6.3)$$

Thus, the energy is lowered by allowing non-zero amplitude of the spin-density waves when

$$\lambda > 187$$

or
$$r_s = \left(\frac{3}{4\pi}\right)^{\frac{1}{3}} \lambda > 116. \qquad (6.4)$$

This appears to us to be fairly conclusive evidence that spin density waves are not energetically favourable until the electron density becomes very much lower than occurs in real metals. Charge density waves may perhaps lower the energy at higher densities however, (see, for example, Young, 1961).

7. Proton lattice problem (with W. Jones)

We shall now give a brief account of some preliminary work
we have carried out on the non-uniform electron gas problem.
Whereas, in the Sommerfeld model, the 'natural' orbitals of the
theory are plane waves for all electron densities, in the case of
a periodic lattice, the 'natural' orbitals will vary with density.
This is an added complication, and has led us to investigate how
we should obtain the Bloch orbitals for a given density. This
seems possible at present only in the limits of high and low
density, and we shall restrict our discussion to these cases.
We should remark at this point that the ground-state energy of
an electron gas in a lattice of positive point charges has been
studied by Bellemans and de Leener (1961). These workers
expanded the grand partition function of the system in powers of
the coupling parameter between the electrons and the positive
point charges and between pairs of electrons. By summing
infinite series of divergent terms they were able to obtain
finite results for the energy per particle.

We have restricted ourselves up to the present to the
calculation of Dirac's matrix in the high-density limit. Thus,
we cannot expect to obtain an energy which includes the Gell-Mann-
Brueckner correlation energy, in contrast to Bellemans and
de Leener. However, we shall demonstrate that there is an
intimate connection between their approach and that given below.

We shall work in a Hartree approximation at first, and shall write the periodic self-consistent potential $V(\underline{r})$ in the form

$$V(\underline{r}) = \sum_{\underline{\kappa}_n} V_{\underline{\kappa}_n} e^{i\underline{\kappa}_n \cdot \underline{r}}, \qquad (7.1)$$

where the $\underline{\kappa}_n$'s are reciprocal lattice vectors. We now make use of the first-order equation of March and Murray (1961), which we may write as

$$\rho(\underline{r}, \zeta) = \frac{k_f^3}{3\pi^2} - \frac{k_f^2}{2\pi^3} \sum_{\underline{\kappa}_n} e^{i\underline{\kappa}_n \cdot \underline{r}} V_{\underline{\kappa}_n} \int e^{i\underline{\kappa}_n \cdot \underline{r}} \frac{j_1(2k_f r)}{r^2} d\underline{r} \qquad (7.2)$$

where the Fermi wave vector has magnitude k_f and is related to the Fermi energy ζ by $k_f^2 = 2\zeta$. Now if the parameter λ measures the magnitude of the positive point charges at the lattice sites $\underline{R}_n$, then

$$\nabla^2 V(\underline{r}) = \lambda \sum_{\underline{R}_n} \delta(\underline{r} - \underline{R}_n) - 4\pi\rho$$

$$= \frac{\lambda}{\Omega} \sum_{\underline{\kappa}_n} e^{i\underline{\kappa}_n \cdot \underline{r}} - 4\pi\rho, \qquad (7.3)$$

where Ω is the volume of a unit cell. Hence, substituting (7.1) and (7.2) in (7.3) we may write

$$-\sum_{\underline{\kappa}_n} \kappa_n{}^2 \, V_{\underline{\kappa}_n} \, e^{i\underline{\kappa}_n\cdot\underline{r}} = \frac{\lambda}{\Omega} \sum_{\underline{\kappa}_n} e^{i\underline{\kappa}_n\cdot\underline{r}} - 4\pi \left(\frac{k_f{}^3}{3\pi^2} - \frac{k_f{}^2}{2\pi^3} \right. \times$$

$$\left. \sum_{\underline{\kappa}_n} e^{i\underline{\kappa}_n\cdot\underline{r}} \, V_{\underline{\kappa}_n} \int e^{i\underline{\kappa}_n\cdot\underline{r}} \, \frac{j_1(2k_f r)}{r^2} \, d\underline{r} \right). \tag{7.4}$$

Hence, for $\underline{\kappa}_n \neq 0$, we have

$$V_{\underline{\kappa}_n} \left\{ \kappa_n{}^2 + \frac{2k_0{}^2}{\pi^2} \int e^{i\underline{\kappa}_n\cdot\underline{r}} \, \frac{j_1(2k_f r)}{r^2} \, d\underline{r} \right\} = -\frac{\lambda}{\Omega}. \tag{7.5}$$

Now

$$\int e^{i\underline{\kappa}_n\cdot\underline{r}} \, \frac{j_1(2k_f r)}{r^2} \, d\underline{r} = \left(\frac{\pi}{2k_f} \right)^{\frac{1}{2}} \int e^{i\underline{\kappa}_n\cdot\underline{r}} \, \frac{J_{\frac{3}{2}}(2k_f r)}{r^{\frac{5}{2}}} \, d\underline{r}$$

$$= \frac{1}{4k_0{}^2} \int e^{i\underline{\kappa}_n\cdot\underline{r}} \, \frac{\{\sin 2k_f r - 2k_f r \cos 2k_f r\}}{r^4} \, d\underline{r}$$

$$= \frac{\pi}{k_f{}^2 \kappa_n} \, J(k_f, \kappa_n) \tag{7.6}$$

where

$$J(k_f, \kappa_n) = \kappa_n k_f + \left(k_f{}^2 - \frac{\kappa_n{}^2}{4} \right) \ell n \left| \frac{2k_f + \kappa_n}{2k_f - \kappa_n} \right|. \tag{7.7}$$

To begin our discussion of the total energy, we first investigate the $E(\underline{k})$ relation in the present approximation. Thus, we write

$$E(\underline{k}) = \sum_{\underline{R}_n} \epsilon_{\underline{R}_n} e^{i\underline{R}_n\cdot\underline{k}}, \tag{7.8}$$

where

$$\epsilon_{\underline{R}_n} = \int_\Omega H\rho(\underline{r}' - \underline{R}_n, \underline{r}) \, d\underline{r}, \qquad (7.9)$$

with the rule that the Hamiltonian H operates only on $\underline{r}$ and we put $\underline{r}' = \underline{r}$ before performing the integration. $\rho(\underline{r}', \underline{r})$ here is the density matrix for the filled band. After some calculation we then find, writing

$$E(\underline{k}) = \frac{k^2}{2} + \Delta E(\underline{k}), \qquad (7.10)$$

that

$$\Delta E(\underline{k}) = -\frac{\Omega_B}{8\pi^3} \sum_{\underline{\kappa}_m} \left| V_{\underline{\kappa}_m} \right|^2 \frac{2}{k_m^2 - k^2} \qquad (7.11)$$

where Ω_B is the volume of the Brillouin zone and $\underline{k}_m = \underline{k} + \underline{\kappa}_m$.

To obtain the change in the sum of the eigenvalues we require

$$\Delta\epsilon = \frac{4}{\Omega_B} \int_{\text{Fermi sphere}} \Delta E(\underline{k}) d\underline{k}$$

$$= -\frac{4}{\Omega_B} \sum_{\underline{\kappa}_m} \left| V_{\underline{\kappa}_m} \right|^2 \int_{\text{Fermi sphere}} \frac{d\underline{k}}{k_m^2 - k^2}$$

$$\qquad (7.12)$$

The integral may be evaluated in terms of the function $J(k_f, \kappa_m)$ defined earlier, and the result may be written

$$\Delta\epsilon = -\frac{2\pi}{\Omega_B} \sum_{\underline{\kappa}_m} \left| V_{\underline{\kappa}_m} \right|^2 \frac{J(k_f, \kappa_m)}{\kappa_m}. \qquad (7.13)$$

If we now insert the Fourier components of the unscreened lattice charge into (7.12), that is we put

$$\left| V_{\kappa_m} \right|^2 = \frac{16\pi^2}{\kappa_m^4 \Omega^2} \qquad (7.14)$$

we find, introducing $u = \kappa_n / 2k_f$,

$$\Delta\epsilon = -\frac{1}{12\pi^2} \sum_{\underline{u}} \frac{1}{u^4} \left[\frac{(1 - u^2)}{2u} \ell n \left| \frac{1 + u}{1 - u} \right| \right]. \qquad (7.15)$$

This, in fact, agrees with the last term in the energy as given by Bellemans and de Leener, and means that their energy can be written down directly by straightforward methods, without recourse to their development of the grand partition function. Obviously, our result (7.13) goes beyond their approximation if we insert the correct Fourier components.

We finally note that in the low density limit, the hydrogen atom wave functions must give the solution of the problem. Then it follows that the momentum distribution function, which seems of some importance in following the behaviour of the system as the lattice parameter is varied, has the form

$$I(p) = \frac{32p^2}{\pi(1 + p^2)^4}. \qquad (7.16)$$

It would certainly be of interest to enquire what modifications would occur in this function as the lattice parameter is now decreased. Obviously, a better approximation than e^{-r} to the

localized orbitals is then required, and we are at present considering ways of introducing perturbations having the correct crystal symmetry in order to obtain the form of $I(p)$ away from the point at infinity.

8. Conclusion

For the Sommerfeld model, the physical behaviour of the system in the two limiting cases $r_s \to 0$ and $r_s \to \infty$ is now well established. If, as we believe, a transition occurs at a critical density r_c, then accurate location and description of this is obviously of considerable interest and we are continuing to examine this problem.

Less is known on the non-uniform gas problem particularly in the low-density limit, and, as remarked above, we are investigating crystalline field methods of developing (7.16) for higher densities.

FIGURE I

FIGURE 2

Captions for Figures

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